

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-297945

(43)Date of publication of application : 29.10.1999

---

(51)Int. CI. H01L 27/10

H01L 21/28

H01L 21/8247

H01L 29/788

H01L 29/792

---

(21)Application number : 10-101035 (71)Applicant : OKI ELECTRIC  
IND CO LTD

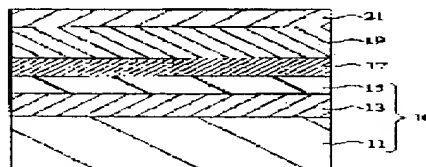
(22)Date of filing : 13.04.1998 (72)Inventor : KOIWA ICHIRO  
KANEHARA  
TAKAO  
KATO HIROYO  
OKADA  
YUKIHISA

---

(54) FERROELECTRIC MEMORY AND MANUFACTURE THEREFOR

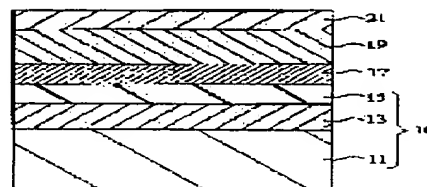
(57)Abstract:

PROBLEM TO BE SOLVED: To  
suppress characteristic  
deterioration of a PZT film due  
to heat treatment in a reducing  
atmosphere, by composing an  
upper electrode of a platinum  
element and one or more kinds of



the elements that compose a lead titanate zirconate film.

SOLUTION: After forming a lead titanate zirconate film 19 by main baking, an upper electrode 21 is formed thereon as a second electrode. The upper electrode 21 is also a platinum electrode. The upper electrode 21 is formed on a ferroelectric film 19 by



sputtering using a platinum target. Then, a structure provided with a lower electrode 17, the ferroelectric film 19 and the upper electrode 21 on a base 10 is heat treated in an oxygen atmosphere. An element which constitutes the film 19, especially lead, is diffused into the upper electrode 21 from the ferroelectric film 19 by the heat treatment. Therefore, the upper electrode 21 becomes an electrode which contains an impurity such as lead. Thus, generation of highly reactive hydrogen atoms is suppressed, and the characteristics of the ferroelectric film are prevented from being deteriorated.

---

#### LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against  
examiner's decision of  
rejection]

[Date of requesting appeal  
against examiner's decision of  
rejection]

[Date of extinction of right]

Copyright (C); 1998, 2003 Japan Patent Office

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**CLAIMS**

---

**[Claim(s)]**

[Claim 1] a kind of the elements with which said up electrode constitutes platinum group metals and said titanate-acid lead zirconate film in the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate containing a semi-conductor substrate, or two sorts or more of elements -- with, the ferroelectric random-access memory characterized by being constituted.

[Claim 2] The element which constitutes said titanate-acid lead zirconate film in said up electrode in ferroelectric random-access memory according to claim 1 is ferroelectric random-access memory characterized by making it spread in the film of said platinum group metals.

[Claim 3] Ferroelectric random-access memory characterized by having had the interlayer who contains a kind or two sorts or more of elements and oxygen in the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate containing a semi-conductor substrate among the elements which constitute this titanate-acid lead zirconate film on said titanate-acid lead zirconate film, and having the up electrode of platinum group metals on this interlayer.

[Claim 4] The ferroelectric-random-access-memory formation approach characterized by to include the process which heat-treats said titanate-acid lead zirconate and an up electrode at least in an oxygen content ambient atmosphere after carrying out the laminating of said lower electrode, the titanate-acid lead-zirconate film, and the up electrode one by one on said substrate in forming the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead-zirconate film, and an up electrode one by one on the substrate containing a semi-conductor substrate, when using said lower electrode and an up

electrode as the electrode of platinum group metals.

[Claim 5] The ferroelectric-random-access-memory formation approach characterized by to include the process which forms said up electrode on said titanate-acid lead-zirconate film by carrying out sputtering in an oxygen content ambient atmosphere using the target of platinum group metals, and a kind of the elements which constitute the titanate-acid lead zirconate film or the target of two or more sorts of elements in forming the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate containing a semi-conductor substrate.

[Claim 6] The ferroelectric-random-access-memory formation approach characterized by including the process which heat-treats said up electrode and the titanate-acid lead zirconate film in an oxygen content ambient atmosphere in the ferroelectric-random-access-memory formation approach according to claim 5 after said sputtering is completed.

[Claim 7] In forming the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate containing a semi-conductor substrate The process which forms the interlayer containing a kind of the elements which constitute this film, or two sorts or more of elements and oxygen on this titanate-acid lead zirconate film after forming a lower electrode and the titanate-acid lead zirconate film on said substrate, The ferroelectric-random-access-memory formation approach characterized by including the process which forms said up electrode on this interlayer.

[Claim 8] The ferroelectric-random-access-memory formation approach characterized by including the process which heat-treats said interlayer and an up electrode in an oxygen content ambient atmosphere at least in the ferroelectric-random-access-memory formation approach according to claim 7 after forming said up electrode on said interlayer.

---

[Translation done.]

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode used for ferroelectric random-access memory, and its formation approach.

[0002]

[Description of the Prior Art] In recent years, densification of semiconductor memory is advanced, and recently, what uses a ferroelectric thin film for the capacitor which carries out the are recording storage of the charge attracts attention as shown in reference (the ceramics, Vol.30 (1995), No.6, pp 499-507). In such semiconductor memory, reversal by electric field and its maintenance function of the spontaneous polarization of a ferroelectric are used. For example, there is a thing using the FET (field-effect transistor) component of MFS (Metal-Ferroelectric-Semiconductor) structure as such semiconductor memory conventionally. This component is the structure which carried out the laminating of the up electrode as the ferroelectric thin film and gate electrode as an insulator layer to the channel field of usual FET one by one. The memory cell using this component reverses polarization of a ferroelectric thin film by impressing an electrical potential difference to between a gate electrode and a semi-conductor substrate (i.e., a ferroelectric thin film). According to the polarization, the channel field of a transistor is made to carry out induction of an electron or the electron hole, and the threshold electrical potential difference of a transistor is changed. The information memorized with the magnitude of the drain current value at this time is identified.

[0003] Moreover, as an ingredient of a ferroelectric thin film, the titanate-acid lead zirconate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ) thin film (however,  $0 < x < 1$ ) with a high dielectric constant (the PZT film is called hereafter.) is used well.

[0004] Moreover, the platinum which is chemically stable and is excellent also in

thermal resistance as an ingredient of an up electrode is used well.

[0005]

[Problem(s) to be Solved by the Invention] However, in manufacturing actually the semiconductor memory (ferroelectric random-access memory) using this PZT film, in that production process, the process which forms an interlayer insulation film, passivation, and a mould is included. At these processes, heat treatment under reducing atmosphere, especially heat treatment in a hydrogen gas content ambient atmosphere are performed. The PZT film which is an oxide will be returned by this heat treatment. Consequently, it becomes the cause of property degradation that film fatigue arises.

[0006] In ferroelectric random-access memory, the platinum which is chemically stable and is excellent in thermal resistance is usually used as an electrode material whose ferroelectric thin film is pinched. However, if heat treatment in a hydrogen gas content ambient atmosphere is performed to the structure equipped with the platinum electrode for ferroelectric random-access memory, this platinum will absorb hydrogen in an atomic form in that grid. This hydrogen atom will have high reactivity and will return the PZT film which is in contact with the platinum electrode from near an interface with a platinum electrode.

[0007] This contained platinum group metals, such as platinum desirable as an electrode material, and an appearance of the ferroelectric random-access memory equipped with the up electrode which can control property degradation of the PZT film by heat treatment in reducing atmosphere, and its formation approach was desired.

[0008]

[Means for Solving the Problem] for this reason, a kind of the elements with which according to the ferroelectric random-access memory of this invention it has a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate containing a semi-conductor substrate at this order, and an up electrode constitutes platinum group metals and the titanate-acid lead zirconate film, or two sorts or more of elements -- with, it is constituted.

[0009] It is lost that the ferroelectric film is returned and a membranous property deteriorates the ferroelectric random-access memory which has such an up electrode even if it processes heat treatment etc. in reducing atmosphere. Since this is the electrode with which an impurity called the element which constitutes not an electrode but the titanate-acid lead zirconate film with which the up electrode consisted of only platinum group metals was contained, the property of absorbing the hydrogen in an ambient atmosphere of the electrode of platinum group metals, and generating a reactant high hydrogen atom has deteriorated. For this reason, it can suppress that the titanate-acid lead zirconate film which is

ferroelectric film is returned by the reactant high hydrogen atom. Therefore, degradation of the property of the ferroelectric film by processing within reducing atmosphere can be prevented. In addition, the element which constitutes the titanate-acid lead zirconate film included in platinum group metals is good also as two or more sorts also as a kind. Moreover, since the impurity contained in an up electrode is an element which constitutes the titanate-acid lead zirconate film, a fear of being polluted with this impurity does not have the titanate-acid lead zirconate film which is in contact with the up electrode.

[0010] Moreover, it is good to make into lead, titanium, or a zirconium preferably elements other than the platinum group metals which constitute an up electrode.

[0011] If an up electrode is made to contain a kind of these, or two sorts or more, it can suppress that a reactant high hydrogen atom occurs in this up electrode.

Moreover, even if a constituent is spread from an up electrode into the titanate-acid lead zirconate film prepared in contact with this up electrode, since it is the component which constitutes this film, it is not polluted into.

[0012] Moreover, in an up electrode, the element which constitutes the titanate-acid lead zirconate film is good to make it spread in the film of platinum group metals. If the element which constitutes the titanate-acid lead zirconate film in an electrode contains in the form of diffusion, the property which absorbs the hydrogen of an electrode can be degraded.

[0013] Moreover, let the platinum group metals used by this invention be one kind of element chosen from the element group of Pt, Ru, Rh, Pd, Os, and Ir.

[0014] Moreover, in the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, it is good to have the interlayer who contains a kind or two sorts or more of elements and oxygen preferably among the elements which constitute the titanate-acid lead zirconate film between the titanate-acid lead zirconate film and an up electrode. In addition, let the up electrode and lower electrode of this ferroelectric random-access memory be the electrode of platinum group metals excellent in chemical stability and thermal resistance.

[0015] Since the middle class is formed between this up electrode and the titanate-acid lead zirconate film although a reactant high hydrogen atom occurs in an up electrode when setting such ferroelectric memory in reducing atmosphere, it can prevent the titanate-acid lead zirconate film being returned by the hydrogen atom. Therefore, degradation of the property of the titanate-acid lead zirconate film resulting from a hydrogen atom can be prevented. Moreover, since this middle class contains oxygen and the constituent of the titanate-acid lead zirconate film, there is no possibility of polluting the titanate-acid lead zirconate film by heat treatment performed into the production process of ferroelectric



random-access memory even if the component of an interlayer is spread on the titanate-acid lead zirconate film. In addition, this middle class's thickness is good to make it thickness which does not insulate an up electrode and the titanate-acid lead zirconate film. Even if thick, it considers as the thickness of 50nm. It is good to consider as the thickness of about 20nm preferably.

[0016] Moreover, after carrying out the laminating of the lower electrode of these platinum group metals, the titanate-acid lead zirconate film, and the up electrode of platinum group metals one by one on a substrate in manufacturing the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, it is good to include the process which heat-treats the titanate-acid lead zirconate film and an up electrode at least in an oxygen content ambient atmosphere.

[0017] By this heat-treatment, titanium and the zirconium in the titanate-acid lead zirconate film, and lead are spread in an up electrode. For this reason, since an impurity will contain in an up electrode, the property of absorbing the hydrogen in the ambient atmosphere of an up electrode, and generating a reactant high hydrogen atom can be degraded. Therefore, it can suppress that the titanate-acid lead zirconate film is returned by the reactant high hydrogen atom. Therefore, the resistance over the reducing atmosphere of ferroelectric random-access memory can be raised.

[0018] Moreover, it is the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, and in manufacturing ferroelectric memory by which the up electrode is constituted from platinum group metals and an element which constitutes the titanate-acid lead zirconate film, it is good [ an up electrode ] to be formed by carrying out sputtering in an oxygen content ambient atmosphere using the target of platinum group metals, and the target of the element which constitutes the titanate-acid lead zirconate film.

[0019] Thereby, the up electrode which titanium and the zirconium which constitute the titanate-acid lead zirconate film, and lead contained can be formed into platinum group metals. For this reason, since an up electrode turns into a platinum electrode which not only platinum group metals but the impurity contained, generating of the reactant high hydrogen atom in an electrode can be suppressed. Thereby, since reduction of the titanate-acid lead zirconate film by the hydrogen atom is suppressed, a possibility of degrading a membranous property disappears.

[0020] Moreover, preferably, after sputtering is completed, it is good in an oxygen content ambient atmosphere to include the process which heat-treats an up electrode and the titanate-acid lead zirconate film.

[0021] Thereby, the constituent of the titanate-acid lead zirconate film is spread from the titanate-acid lead zirconate film to an up electrode. Therefore, since an impurity is further introduced into an up electrode, the property which absorbs the hydrogen of platinum group metals deteriorates, and generating of a reactant high hydrogen atom can be controlled more. In addition, the ambient atmosphere containing 20% of oxygen of atmospheric-air extent is sufficient as an oxygen content ambient atmosphere. Thereby, an up electrode can be made to contain an impurity, without making the titanate-acid lead zirconate film return. Moreover, many rates which oxygen contains in this ambient atmosphere are so good that there are, and good to consider as 100% or less 20% or more.

[0022] Moreover, after forming a lower electrode and the titanate-acid lead-zirconate film on a substrate in manufacturing the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate, it is good to include the process which forms the interlayer containing a kind of the elements which constitute this film, or two sorts or more of elements and oxygen on this titanate-acid lead-zirconate film, and the process which forms an up electrode on this interlayer.

[0023] Since what is the easiest to be returned is near the interface of the ferroelectric film and an up electrode when using an up electrode as the electrode of platinum group metals, and a reactant high hydrogen atom occurs with an up electrode, if the middle class containing oxygen is prepared between this ferroelectric film and an up electrode, it can prevent the middle class's turning into a barrier layer and the ferroelectric film being returned by the hydrogen atom.

[0024] Moreover, after forming an up electrode, this interlayer and an up electrode are heat-treated in an oxygen content ambient atmosphere.

[0025] Thereby, the element which constitutes the ferroelectric film from an interlayer to an up electrode is spread. Therefore, since an impurity is introduced into the up electrode of platinum group metals, the property of absorbing the hydrogen of platinum group metals and generating a reactant high hydrogen atom deteriorates. in an up electrode, even if there is a process which heat-treats in reducing atmosphere behind in the formation process of ferroelectric random-access memory by this, since generating of a reactant high hydrogen atom is controlled, the titanate-acid lead zirconate film which is ferroelectric film is returned by this hydrogen, and a property deteriorates by it -- it can protect. Since the interlayer intervenes between an up electrode and the ferroelectric film even if a hydrogen atom occurs with an up electrode, there is no possibility that the ferroelectric film may be returned. Moreover, the ambient atmosphere

containing 20% of oxygen of atmospheric-air extent is sufficient as an oxygen content ambient atmosphere. Thereby, into an up electrode, the element which constitutes the ferroelectric film from an interlayer is introduced as an impurity, without returning the titanate-acid lead zirconate film. Moreover, more ones of the rate which this oxygen contains are desirable, and it is good to consider as 100% or less 20% or more.

[0026] This interlayer may be 50nm, even if it is good to make it thickness which does not insulate an up electrode and the ferroelectric film and it is thick. And desirable thickness is about 20nm.

[0027]

[Embodiment of the Invention] Hereafter, with reference to drawing, it explains per gestalt of implementation of this invention. In addition, each drawing is not passed for it to be roughly shown in extent which can understand invention, and be, therefore does not limit invention to the example of a graphic display.

[0028] Moreover, it does not pass over the ingredient or the numerical conditions of being used with the gestalt of this operation, to an example of this invention within the limits, and, therefore, invention is not limited only to these conditions.

[0029] <the gestalt of the 1st operation> -- with reference to drawing 1 , it explains about the sample of the ferroelectric random-access memory of this invention as a gestalt of implementation of the 1st of this invention. Drawing 1 is drawing showing the cut end of the cross section which showed roughly the structure of the sample of the ferroelectric random-access memory of this invention.

[0030] First, the sample of the ferroelectric random-access memory of the gestalt of this operation is formed. The substrate 10 of this sample is made into the substrate excellent in an electrode, adhesion, and thermal resistance. Here, on a silicon substrate 11, one by one, it is a spin coater, with the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out. These three layers (a silicon substrate 11, the polish recon layer 13, and TiN barrier layer 15) are used as a substrate 10.

[0031] Next, the lower electrode 17 is formed as the 1st electrode on this substrate 10. Here, the lower electrode 17 is used as a platinum electrode, and the lower electrode 17 is formed by sputtering using the platinum target used by the usual electrode formation.

[0032] Next, the ferroelectric film 19 is formed on this lower electrode 17.

[0033] With the gestalt of this operation, the spreading film of titanate-acid lead zirconate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (however,  $0 < x < 1$ )) is formed by the spin coater on the above-mentioned electrode 17, for example. Then, after drying this spreading

film and evaporating the solvent in the spreading film, temporary baking is performed to the spreading film and an organic functional group is burned. Then, this baking is performed and the titanate-acid lead zirconate film 19 is formed.

[0034] Then, the up electrode 21 is formed as the 2nd electrode on the ferroelectric film 19.

[0035] Also let the up electrode 21 be a platinum electrode with the gestalt of this operation. Therefore, the up electrode 21 is formed on the ferroelectric film 19 like formation of the lower electrode 17 performing sputtering using a platinum target.

[0036] Then, with the gestalt of this operation, the structure equipped with the lower electrode 17, the ferroelectric film 19, and the up electrode 21 on the substrate 10 is heat-treated in an oxygen ambient atmosphere. Here, heat-treatment is performed at the temperature of 800 degrees C for 30 minutes in a pure oxygen ambient atmosphere (inside of about 100% oxygen ambient atmosphere).

[0037] The element which constitutes this film 19 from ferroelectric film 19 in the up electrode 21, especially lead are spread by this heat treatment. For this reason, the up electrode 21 turns into an electrode containing impurities, such as lead.

[0038] Thereby, the sample of the gestalt of this operation is formed (refer to drawing 1 ). According to this, the lower electrode 17, the ferroelectric film 19, and the up electrode 21 are formed on the substrate 10 at this order. And this up electrode 21 is a platinum electrode which the constituent of the ferroelectric film 19, such as lead, has diffused.

[0039] Here, it explains briefly about the trouble of the platinum electrode used so far. A platinum electrode has the property of absorbing hydrogen and generating a reactant high hydrogen atom in reducing atmosphere, especially the ambient atmosphere containing hydrogen. This hydrogen atom had become the cause which causes degradation of film fatigue of the ferroelectric film etc. in order to make the ferroelectric film return.

[0040] In manufacturing ferroelectric random-access memory, heat treatment under the ambient atmosphere of reducibility is performed by the process which forms an interlayer insulation film behind, the formation process of the passivation film, etc. For this reason, the property of the platinum electrode which made the impurity contain, then the platinum electrode which absorbs hydrogen can be degraded like the up electrode of the gestalt of this operation. Since generating of a reactant high hydrogen atom is also suppressed by this, even if it performs heat treatment by reducing atmosphere which contains hydrogen, a possibility of degrading the property of the ferroelectric film

disappears.

[0041] In addition, although a lower electrode is also a platinum electrode, in the lower electrode, the film constituent in the ferroelectric film is spread by heat treatment performed when forming the ferroelectric film. For this reason, when forming an up electrode, there is already no fear of originating in this lower electrode and degrading the property of the ferroelectric film, since the absorption property of hydrogen has deteriorated.

[0042] With reference to drawing 1 and drawing 2 , it explains about the sample of the ferroelectric random-access memory of the gestalt of <gestalt of the 2nd operation> the 2nd operation. Drawing 2 is the top view of the field where the sputtering gas of the target used when performing sputtering with the gestalt of this operation collides. As for this sample, the up electrode as the lower electrode, the ferroelectric film, and the 2nd electrode as the 1st electrode is prepared on the substrate, and these are manufactured almost like the gestalt of the 1st operation. Moreover, although drawing 1 is the block diagram of the sample of the gestalt of the 1st operation, since the 2nd configuration of the sample of the gestalt of operation is almost the same as the sample of the gestalt of the 1st operation, it explains by using this drawing 1 . In addition, in the sample of the gestalt of this operation, the constituent of an up electrode differs from the gestalt of the 1st operation.

[0043] It explains hereafter per [ which is different from the gestalt of the 1st operation ] point, and the detailed explanation is omitted about the same point as the gestalt of the 1st operation.

[0044] First, like the gestalt of the 1st operation, on a silicon substrate 11, the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out one by one, and a substrate 10 is formed.

[0045] Next, after forming the lower electrode 17 of platinum as the 1st electrode like the gestalt of the 1st operation on this substrate 10, the titanate-acid lead zirconate film is formed as ferroelectric film 19 on the lower electrode 17.

[0046] Next, the up electrode 21 is formed as the 2nd electrode on this ferroelectric film 19.

[0047] With the gestalt of this operation, the up electrode 21 is formed on the ferroelectric film 19 by carrying out sputtering in an oxygen content ambient atmosphere using the target 30 of platinum and lead.

[0048] the lead 33 of the shape of a sheet whose thickness it is 1mm around on the 6 inches (however, 1 inch about 2.54cm) platinum target 31, and is 2mm here -- 17 sheets -- mutual -- etc. -- carrying out -- it is -- spacing -- with, it arranges (refer to drawing 2 ). As for this lead sheet 33, purity uses 99.99% or more of

thing. Moreover, an area of one sheet of the lead sheet 33 is made into about 5% of the area of the platinum target 31. In order to make it not degrade the crystallinity of platinum, as for the area of the lead sheet 33, it is desirable to carry out to about 5% of the platinum target 31 as mentioned above. Moreover, what is necessary is just to carry the lead sheet 33 on the platinum target 31. Thus, what has arranged the lead sheet 33 is used as a target 30 on the platinum target 31.

[0049] Next, sputtering is performed in an oxygen content ambient atmosphere using this target 30.

[0050] Alignment of the substrate 10 equipped with a target 30, the ferroelectric film 19, and the lower electrode 17 is carried out, and it installs in a sputtering system. Sputtering is performed using the argon sputtering gas containing oxygen 10 capacity %. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time. After performing a pre spatter for 2 minutes, the platinum electrode 21 containing the lead whose thickness is 200nm and which is about 10% is formed on the ferroelectric film 19 by opening and carrying out sputtering of the shutter for 3 minutes.

[0051] Thereby, the sample of the gestalt of this operation is formed (refer to drawing 1 ).

[0052] As the gestalt of the 1st operation explained, a platinum electrode has a possibility of generating a reactant high hydrogen atom and returning the ferroelectric film, in heat treatment under the ambient atmosphere of reducibility. And reduction of the ferroelectric film has arisen mainly from the interface of an up electrode and the ferroelectric film.

[0053] With the gestalt of this operation, the platinum electrode which lead contained is used as an up electrode. In other words, an impurity called lead is contained in the platinum electrode. For this reason, the property which absorbs the hydrogen of a platinum electrode has deteriorated. Therefore, since generating of a reactant high hydrogen atom can be suppressed in connection with this, even if it performs heat treatment by reducing atmosphere which contains hydrogen, a possibility of degrading the property of the ferroelectric film disappears.

[0054] Moreover, in this up electrode, if lead is contained about 2% to about 20%, effectiveness will be acquired as an impurity. That is, the property of absorbing the hydrogen in the reducing atmosphere of a platinum electrode, and generating a reactant high hydrogen atom can be degraded. It is good to consider as 10% preferably as a rate which lead contains.

[0055] Moreover, although there is a possibility that a constituent may be spread

from an up electrode and the ferroelectric film may be polluted with heat treatment performed into the production process of ferroelectric random-access memory, since an up electrode is an electrode which consisted of platinum and lead which is the constituent of the titanate-acid lead zirconate film of the ferroelectric film, there is no possibility of making the ferroelectric film polluting here.

[0056] Moreover, although lead and platinum constituted the up electrode from the gestalt of this operation, you may constitute from Ti and platinum which are the constituent of the titanate-acid lead zirconate film, and the same effectiveness is acquired even if constituted from a zirconium and platinum.

[0057] Moreover, with the gestalt of this operation, although platinum is used for the ingredient of an electrode, \*\*\*\*\* of Ru, Rh(s), Pd, Os(es), and Ir(s) which are the platinum group which has the same property as platinum may be used as an electrode material. Especially, Ir and Ru are easy to etch compared with platinum, and since it excels in workability, it is thought that it is an ingredient desirable as an electrode material.

[0058] It heat-treats in an oxygen content ambient atmosphere to the sample of the ferroelectric random-access memory formed with the gestalt of <gestalt of the 3rd operation> the 2nd operation.

[0059] As the gestalt of the 2nd operation explained, after carrying out the laminating of a polish recon layer and the TiN barrier layer one by one and forming a substrate on a silicon substrate, on this substrate, sequential formation of the up electrode as the 2nd electrode containing the lower electrode, the titanate-acid lead zirconate film and platinum, and lead of platinum as the 1st electrode is carried out, and a sample is formed.

[0060] Then, in the gestalt of this operation, after putting in this sample into the ambient atmosphere which is about 100% oxygen, heat-treatment is performed at the temperature of 800 degrees C for 30 minutes.

[0061] Consequently, in an up electrode, the component which constitutes this film is further spread from the ferroelectric film. Therefore, the property which absorbs the hydrogen of an up electrode can be degraded further. Thereby, further improvement in the resistance of the ferroelectric film to heat treatment by reducing atmosphere can be aimed at.

[0062] if extent as atmospheric air with the same oxygen contains the oxygen content ambient atmosphere of heat-treating, 20% or more -- \*\*\*\* -- \*\*\*\*ing . As the rate which oxygen contains is high, it is more desirable.

[0063] Moreover, in the gestalt of this operation, although temperature of heat-treatment was made into 800 degrees C, it can carry out at the temperature of 600 degrees C - 850 degrees C. It is good to heat-treat preferably at the

temperature within the limits of 750 degrees C - 800 degrees C.

[0064] With reference to drawing 3 , it explains about the sample of the ferroelectric random-access memory of the gestalt of <gestalt of the 4th operation> the 4th operation. Drawing 3 is the sectional view showing the 4th rough configuration of the sample of the gestalt of operation.

[0065] It explains hereafter per [ which is different from the gestalt of the 1st - the 3rd operation ] point, and the detailed explanation is omitted about the same point.

[0066] As for this sample, the up electrode 21 is formed as the lower electrode 17, the ferroelectric film 19, and the 2nd electrode as the 1st electrode on the substrate 10. Furthermore, the interlayer 23 who contains a kind or two sorts or more of elements and oxygen among the elements which constitute the ferroelectric film 19 is formed between the ferroelectric film 19 and the up electrode 21 ( drawing 3 ).

[0067] This sample is manufactured as follows.

[0068] Like the gestalt of the 1st operation, on a silicon substrate 11, the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out one by one, and a substrate 10 is formed.

[0069] Next, like the gestalt of the 1st operation, after forming the lower electrode 17 of platinum, the titanate-acid lead zirconate film is formed as ferroelectric film 19 on this lower electrode 17.

[0070] Then, the interlayer 23 containing lead and oxygen is formed with the gestalt of this operation.

[0071] Here, sputtering is performed in an oxygen content ambient atmosphere using a 6 inches lead target. Bi target and the structure by which the lower electrode 17 and the ferroelectric film 19 were formed on the substrate 10 are installed in a sputtering system, and sputtering is performed using the argon sputtering gas containing oxygen 10 capacity %. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time. After performing a pre spatter for 2 minutes, the interlayer 23 containing 20nm lead and oxygen is formed on the ferroelectric film 19 by opening and carrying out sputtering of the shutter for 20 seconds.

[0072] Then, sputtering is performed using the argon sputtering gas containing oxygen 10 capacity % using a 6 inches platinum target. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time.

[0073] After performing a pre spatter for 2 minutes, a shutter is opened,



sputtering is performed for 3 minutes, and the up electrode 21 of platinum with a thickness of 200nm is obtained.

[0074] Thereby, the sample of the gestalt of the 4th operation is formed (refer to drawing 3 ).

[0075] When an interlayer insulation film and the passivation film tend to be further formed in this sample and it is going to manufacture ferroelectric random-access memory, the process which performs heat treatment under reducing atmosphere is not avoided. Under reducing atmosphere which contains hydrogen, the up electrode of platinum absorbs the hydrogen in an ambient atmosphere, and generates a reactant high hydrogen atom. This hydrogen atom makes the ferroelectric film return, and has become one of the causes which degrades the property of film, such as film fatigue. What is easy to be influenced of a reactant high hydrogen atom, namely, is easy to be returned is near the interface of the ferroelectric film and an up electrode.

[0076] For this reason, if the layer containing oxygen is prepared between the ferroelectric film 19 and the up electrode 21 as an interlayer 23 like the gestalt of this operation, it can prevent that inside [ this ] \*\*\*\* 23 turns into a barrier layer, and a hydrogen atom attains to the ferroelectric film 19 from the up electrode 21. Therefore, even if it performs heat treatment by reducing atmosphere, degradation of the property of the ferroelectric film 19 can be controlled.

[0077] Moreover, even if this interlayer's 23 thickness is thick, it is good to be referred to as 50nm. If it is 50nm or less in thickness, the up electrode 21 and the ferroelectric film 19 are not insulated by the interlayer 23 who is an oxide film, and the effect of the hydrogen atom from the up electrode 21 to the ferroelectric film 19 can be controlled.

[0078] Moreover, the middle class 23 is a layer containing the lead of the constituent of the titanate-acid lead zirconate film which is the ferroelectric film 19. For this reason, even if the component which constitutes an interlayer 23 from an interlayer 23 to the ferroelectric film 19 is spread by heat treatment performed into a ferroelectric-random-access-memory production process, there is no possibility that the ferroelectric film 19 may be polluted.

[0079] Moreover, the effectiveness that the middle class 23 is the same also as the layer containing Ti which constitutes not only the layer containing lead and oxygen but the titanate-acid lead zirconate film 19, and oxygen, or a layer containing a zirconium and oxygen is acquired.

[0080] Moreover, in the gestalt of this operation, although the up electrode 21 is used as the platinum electrode, it is good also as an electrode of Ru, Rh, Pa, Os, and Ir which are the platinum group metals which have the same property not only as this but platinum.

[0081] It heat-treats in an oxygen content ambient atmosphere to the sample of the ferroelectric random-access memory formed with the gestalt of <gestalt of the 5th operation> the 4th operation.

[0082] As the gestalt of the 4th operation explained, after carrying out the laminating of a polish recon layer and the TiN barrier layer one by one and forming a substrate on a silicon substrate, on this substrate, sequential formation of the lower electrode of platinum, the titanate-acid lead zirconate film, an interlayer, and the up electrode of platinum is carried out, and a sample is formed.

[0083] Then, in the gestalt of this operation, after putting in this sample into the ambient atmosphere of about 100% oxygen, heat-treatment is performed for 30 minutes at the temperature of 800 degrees C.

[0084] Consequently, lead is spread from an interlayer in an up electrode. For this reason, since an impurity is introduced into the up electrode of platinum, the property which absorbs the hydrogen of a platinum electrode can be degraded. Therefore, since generating of a reactant high hydrogen atom can be suppressed, even if it heat-treats to this sample in reducing atmosphere, the ferroelectric film can control degradation of the film accompanying this, without being returned. Even if a hydrogen atom occurs, the effect of the hydrogen atom to the ferroelectric film can be suppressed by the interlayer.

[0085] if extent as atmospheric air with the same oxygen contains the oxygen content ambient atmosphere of heat-treating, 20% or more -- \*\*\*\* -- \*\*\*\*ing . As the rate which oxygen contains is high, it is more desirable.

[0086] Moreover, in the gestalt of this operation, although temperature of heat-treatment was made into 800 degrees C, it can carry out at the temperature of 600 degrees C - 850 degrees C. It is good to heat-treat preferably at the temperature within the limits of 750 degrees C - 800 degrees C.

[0087] In the sample of the ferroelectric random-access memory of the gestalt of this operation, although platinum is used for the ingredient of an electrode, platinum group metals, such as not only this but Ru, Ir, etc., may be used.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[Field of the Invention] This invention relates to the electrode used for ferroelectric random-access memory, and its formation approach.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

PRIOR ART

---

[Description of the Prior Art] In recent years, densification of semiconductor memory is advanced, and recently, what uses a ferroelectric thin film for the capacitor which carries out the are recording storage of the charge attracts attention as shown in reference (the ceramics, Vol.30 (1995), No.6, pp 499-507). In such semiconductor memory, reversal by electric field and its maintenance function of the spontaneous polarization of a ferroelectric are used. For example, there is a thing using the FET (field-effect transistor) component of MFS (Metal-Ferroelectric-Semiconductor) structure as such semiconductor memory conventionally. This component is the structure which carried out the laminating of the up electrode as the ferroelectric thin film and gate electrode as an insulator layer to the channel field of usual FET one by one. The memory cell using this component reverses polarization of a ferroelectric thin film by impressing an electrical potential difference to between a gate electrode and a semi-conductor substrate (i.e., a ferroelectric thin film). According to the polarization, the channel field of a transistor is made to carry out induction of an electron or the electron hole, and the threshold electrical potential difference of a transistor is changed. The information memorized with the magnitude of the drain current value at this time is identified.

[0003] Moreover, as an ingredient of a ferroelectric thin film, the titanate-acid lead zirconate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ) thin film (however,  $0 < x < 1$ ) with a high dielectric constant (the PZT film is called hereafter.) is used well.

[0004] Moreover, the platinum which is chemically stable and is excellent also in thermal resistance as an ingredient of an up electrode is used well.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention] However, in manufacturing actually the semiconductor memory (ferroelectric random-access memory) using this PZT film, in that production process, the process which forms an interlayer insulation film, passivation, and a mould is included. At these processes, heat treatment under reducing atmosphere, especially heat treatment in a hydrogen gas content ambient atmosphere are performed. The PZT film which is an oxide will be returned by this heat treatment. Consequently, it becomes the cause of property degradation that film fatigue arises.

[0006] In ferroelectric random-access memory, the platinum which is chemically stable and is excellent in thermal resistance is usually used as an electrode material whose ferroelectric thin film is pinched. However, if heat treatment in a hydrogen gas content ambient atmosphere is performed to the structure equipped with the platinum electrode for ferroelectric random-access memory, this platinum will absorb hydrogen in an atomic form in that grid. This hydrogen atom will have high reactivity and will return the PZT film which is in contact with the platinum electrode from near an interface with a platinum electrode.

[0007] This contained platinum group metals, such as platinum desirable as an electrode material, and an appearance of the ferroelectric random-access memory equipped with the up electrode which can control property degradation of the PZT film by heat treatment in reducing atmosphere, and its formation approach was desired.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

MEANS

---

[Means for Solving the Problem] for this reason, a kind of the elements with which according to the ferroelectric random-access memory of this invention it has a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate containing a semi-conductor substrate at this order, and an up electrode constitutes platinum group metals and the titanate-acid lead zirconate film, or two sorts or more of elements -- with, it is constituted.

[0009] It is lost that the ferroelectric film is returned and a membranous property deteriorates the ferroelectric random-access memory which has such an up electrode even if it processes heat treatment etc. in reducing atmosphere. Since this is the electrode with which an impurity called the element which constitutes not an electrode but the titanate-acid lead zirconate film with which the up electrode consisted of only platinum group metals was contained, the property of absorbing the hydrogen in an ambient atmosphere of the electrode of platinum group metals, and generating a reactant high hydrogen atom has deteriorated. For this reason, it can suppress that the titanate-acid lead zirconate film which is ferroelectric film is returned by the reactant high hydrogen atom. Therefore, degradation of the property of the ferroelectric film by processing within reducing atmosphere can be prevented. In addition, the element which constitutes the titanate-acid lead zirconate film included in platinum group metals is good also as two or more sorts also as a kind. Moreover, since the impurity contained in an up electrode is an element which constitutes the titanate-acid lead zirconate film, a fear of being polluted with this impurity does not have the titanate-acid lead zirconate film which is in contact with the up electrode.

[0010] Moreover, it is good to make into lead, titanium, or a zirconium preferably elements other than the platinum group metals which constitute an up electrode.

[0011] If an up electrode is made to contain a kind of these, or two sorts or more, it can suppress that a reactant high hydrogen atom occurs in this up electrode.

Moreover, even if a constituent is spread from an up electrode into the titanate-acid lead zirconate film prepared in contact with this up electrode, since it is the component which constitutes this film, it is not polluted into.

[0012] Moreover, in an up electrode, the element which constitutes the titanate-acid lead zirconate film is good to make it spread in the film of platinum group metals. If the element which constitutes the titanate-acid lead zirconate film in an electrode contains in the form of diffusion, the property which absorbs the hydrogen of an electrode can be degraded.

[0013] Moreover, let the platinum group metals used by this invention be one kind of element chosen from the element group of Pt, Ru, Rh, Pd, Os, and Ir.

[0014] Moreover, in the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, it is good to have the interlayer who contains a kind or two sorts or more of elements and oxygen preferably among the elements which constitute the titanate-acid lead zirconate film between the titanate-acid lead zirconate film and an up electrode. In addition, let the up electrode and lower electrode of this ferroelectric random-access memory be the electrode of platinum group metals excellent in chemical stability and thermal resistance.

[0015] Since the middle class is formed between this up electrode and the titanate-acid lead zirconate film although a reactant high hydrogen atom occurs in an up electrode when setting such ferroelectric memory in reducing atmosphere, it can prevent the titanate-acid lead zirconate film being returned by the hydrogen atom. Therefore, degradation of the property of the titanate-acid lead zirconate film resulting from a hydrogen atom can be prevented. Moreover, since this middle class contains oxygen and the constituent of the titanate-acid lead zirconate film, there is no possibility of polluting the titanate-acid lead zirconate film by heat treatment performed into the production process of ferroelectric random-access memory even if the component of an interlayer is spread on the titanate-acid lead zirconate film. In addition, this middle class's thickness is good to make it thickness which does not insulate an up electrode and the titanate-acid lead zirconate film. Even if thick, it considers as the thickness of 50nm. It is good to consider as the thickness of about 20nm preferably.

[0016] Moreover, after carrying out the laminating of the lower electrode of these platinum group metals, the titanate-acid lead zirconate film, and the up electrode of platinum group metals one by one on a substrate in manufacturing the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, it is good to include the process which heat-treats the titanate-acid lead zirconate film and an up electrode at least in an oxygen content ambient atmosphere.

[0017] By this heat-treatment, titanium and the zirconium in the titanate-acid lead zirconate film, and lead are spread in an up electrode. For this reason, since an impurity will contain in an up electrode, the property of absorbing the hydrogen in the ambient atmosphere of an up electrode, and generating a reactant high hydrogen atom can be degraded. Therefore, it can suppress that the titanate-acid lead zirconate film is returned by the reactant high hydrogen atom. Therefore, the resistance over the reducing atmosphere of ferroelectric random-access memory can be raised.

[0018] Moreover, it is the ferroelectric random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode on the substrate at this order, and in manufacturing ferroelectric memory by which the up electrode is constituted from platinum group metals and an element which constitutes the titanate-acid lead zirconate film, it is good [ an up electrode ] to be formed by carrying out sputtering in an oxygen content ambient atmosphere using the target of platinum group metals, and the target of the element which constitutes the titanate-acid lead zirconate film.

[0019] Thereby, the up electrode which titanium and the zirconium which constitute the titanate-acid lead zirconate film, and lead contained can be formed into platinum group metals. For this reason, since an up electrode turns into a platinum electrode which not only platinum group metals but the impurity contained, generating of the reactant high hydrogen atom in an electrode can be suppressed. Thereby, since reduction of the titanate-acid lead zirconate film by the hydrogen atom is suppressed, a possibility of degrading a membranous property disappears.

[0020] Moreover, preferably, after sputtering is completed, it is good in an oxygen content ambient atmosphere to include the process which heat-treats an up electrode and the titanate-acid lead zirconate film.

[0021] Thereby, the constituent of the titanate-acid lead zirconate film is spread from the titanate-acid lead zirconate film to an up electrode. Therefore, since an impurity is further introduced into an up electrode, the property which absorbs the hydrogen of platinum group metals deteriorates, and generating of a reactant high hydrogen atom can be controlled more. In addition, the ambient atmosphere containing 20% of oxygen of atmospheric-air extent is sufficient as an oxygen content ambient atmosphere. Thereby, an up electrode can be made to contain an impurity, without making the titanate-acid lead zirconate film return. Moreover, many rates which oxygen contains in this ambient atmosphere are so good that there are, and good to consider as 100% or less 20% or more.

[0022] Moreover, after forming a lower electrode and the titanate-acid lead-zirconate film on a substrate in manufacturing the ferroelectric



random-access memory equipped with a lower electrode, the titanate-acid lead zirconate film, and an up electrode one by one on the substrate, it is good to include the process which forms the interlayer containing a kind of the elements which constitute this film, or two sorts or more of elements and oxygen on this titanate-acid lead-zirconate film, and the process which forms an up electrode on this interlayer.

[0023] Since what is the easiest to be returned is near the interface of the ferroelectric film and an up electrode when using an up electrode as the electrode of platinum group metals, and a reactant high hydrogen atom occurs with an up electrode, if the middle class containing oxygen is prepared between this ferroelectric film and an up electrode, it can prevent the middle class's turning into a barrier layer and the ferroelectric film being returned by the hydrogen atom.

[0024] Moreover, after forming an up electrode, this interlayer and an up electrode are heat-treated in an oxygen content ambient atmosphere.

[0025] Thereby, the element which constitutes the ferroelectric film from an interlayer to an up electrode is spread. Therefore, since an impurity is introduced into the up electrode of platinum group metals, the property of absorbing the hydrogen of platinum group metals and generating a reactant high hydrogen atom deteriorates. In an up electrode, even if there is a process which heat-treats in reducing atmosphere behind in the formation process of ferroelectric random-access memory by this, since generating of a reactant high hydrogen atom is controlled, the titanate-acid lead zirconate film which is ferroelectric film is returned by this hydrogen, and a property deteriorates by it -- it can protect. Since the interlayer intervenes between an up electrode and the ferroelectric film even if a hydrogen atom occurs with an up electrode, there is no possibility that the ferroelectric film may be returned. Moreover, the ambient atmosphere containing 20% of oxygen of atmospheric-air extent is sufficient as an oxygen content ambient atmosphere. Thereby, into an up electrode, the element which constitutes the ferroelectric film from an interlayer is introduced as an impurity, without returning the titanate-acid lead zirconate film. Moreover, more ones of the rate which this oxygen contains are desirable, and it is good to consider as 100% or less 20% or more.

[0026] This interlayer may be 50nm, even if it is good to make its thickness which does not insulate an up electrode and the ferroelectric film and it is thick. And desirable thickness is about 20nm.

[0027]

[Embodiment of the Invention] Hereafter, with reference to drawing, it explains per gestalt of implementation of this invention. In addition, each drawing is not

passed for it to be roughly shown in extent which can understand invention, and be, therefore does not limit invention to the example of a graphic display.

[0028] Moreover, it does not pass over the ingredient or the numerical conditions of being used with the gestalt of this operation, to an example of this invention within the limits, and, therefore, invention is not limited only to these conditions.

[0029] <the gestalt of the 1st operation> -- with reference to drawing 1 , it explains about the sample of the ferroelectric random-access memory of this invention as a gestalt of implementation of the 1st of this invention. Drawing 1 is drawing showing the cut end of the cross section which showed roughly the structure of the sample of the ferroelectric random-access memory of this invention.

[0030] First, the sample of the ferroelectric random-access memory of the gestalt of this operation is formed. The substrate 10 of this sample is made into the substrate excellent in an electrode, adhesion, and thermal resistance. Here, on a silicon substrate 11, one by one, it is a spin coater, with the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out. These three layers (a silicon substrate 11, the polish recon layer 13, and TiN barrier layer 15) are used as a substrate 10.

[0031] Next, the lower electrode 17 is formed as the 1st electrode on this substrate 10. Here, the lower electrode 17 is used as a platinum electrode, and the lower electrode 17 is formed by sputtering using the platinum target used by the usual electrode formation.

[0032] Next, the ferroelectric film 19 is formed on this lower electrode 17.

[0033] With the gestalt of this operation, the spreading film of titanate-acid lead zirconate ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (however,  $0 < x < 1$ )) is formed by the spin coater on the above-mentioned electrode 17, for example. Then, after drying this spreading film and evaporating the solvent in the spreading film, temporary baking is performed to the spreading film and an organic functional group is burned. Then, this baking is performed and the titanate-acid lead zirconate film 19 is formed.

[0034] Then, the up electrode 21 is formed as the 2nd electrode on the ferroelectric film 19.

[0035] Also let the up electrode 21 be a platinum electrode with the gestalt of this operation. Therefore, the up electrode 21 is formed on the ferroelectric film 19 like formation of the lower electrode 17 performing sputtering using a platinum target.

[0036] Then, with the gestalt of this operation, the structure equipped with the lower electrode 17, the ferroelectric film 19, and the up electrode 21 on the substrate 10 is heat-treated in an oxygen ambient atmosphere. Here,

heat-treatment is performed at the temperature of 800 degrees C for 30 minutes in a pure oxygen ambient atmosphere (inside of about 100% oxygen ambient atmosphere).

[0037] The element which constitutes this film 19 from ferroelectric film 19 in the up electrode 21, especially lead are spread by this heat treatment. For this reason, the up electrode 21 turns into an electrode containing impurities, such as lead.

[0038] Thereby, the sample of the gestalt of this operation is formed (refer to drawing 1 ). According to this, the lower electrode 17, the ferroelectric film 19, and the up electrode 21 are formed on the substrate 10 at this order. And this up electrode 21 is a platinum electrode which the constituent of the ferroelectric film 19, such as lead, has diffused.

[0039] Here, it explains briefly about the trouble of the platinum electrode used so far. A platinum electrode has the property of absorbing hydrogen and generating a reactant high hydrogen atom in reducing atmosphere, especially the ambient atmosphere containing hydrogen. This hydrogen atom had become the cause which causes degradation of film fatigue of the ferroelectric film etc. in order to make the ferroelectric film return.

[0040] In manufacturing ferroelectric random-access memory, heat treatment under the ambient atmosphere of reducibility is performed by the process which forms an interlayer insulation film behind, the formation process of the passivation film, etc. For this reason, the property of the platinum electrode which made the impurity contain, then the platinum electrode which absorbs hydrogen can be degraded like the up electrode of the gestalt of this operation. Since generating of a reactant high hydrogen atom is also suppressed by this, even if it performs heat treatment by reducing atmosphere which contains hydrogen, a possibility of degrading the property of the ferroelectric film disappears.

[0041] In addition, although a lower electrode is also a platinum electrode, in the lower electrode, the film constituent in the ferroelectric film is spread by heat treatment performed when forming the ferroelectric film. For this reason, when forming an up electrode, there is already no fear of originating in this lower electrode and degrading the property of the ferroelectric film, since the absorption property of hydrogen has deteriorated.

[0042] With reference to drawing 1 and drawing 2 , it explains about the sample of the ferroelectric random-access memory of the gestalt of <gestalt of the 2nd operation> the 2nd operation. Drawing 2 is the top view of the field where the sputtering gas of the target used when performing sputtering with the gestalt of

this operation collides. As for this sample, the up electrode as the lower electrode, the ferroelectric film, and the 2nd electrode as the 1st electrode is prepared on the substrate, and these are manufactured almost like the gestalt of the 1st operation. Moreover, although drawing 1 is the block diagram of the sample of the gestalt of the 1st operation, since the 2nd configuration of the sample of the gestalt of operation is almost the same as the sample of the gestalt of the 1st operation, it explains by using this drawing 1. In addition, in the sample of the gestalt of this operation, the constituent of an up electrode differs from the gestalt of the 1st operation.

[0043] It explains hereafter per [ which is different from the gestalt of the 1st operation ] point, and the detailed explanation is omitted about the same point as the gestalt of the 1st operation.

[0044] First, like the gestalt of the 1st operation, on a silicon substrate 11, the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out one by one, and a substrate 10 is formed.

[0045] Next, after forming the lower electrode 17 of platinum as the 1st electrode like the gestalt of the 1st operation on this substrate 10, the titanate-acid lead zirconate film is formed as ferroelectric film 19 on the lower electrode 17.

[0046] Next, the up electrode 21 is formed as the 2nd electrode on this ferroelectric film 19.

[0047] With the gestalt of this operation, the up electrode 21 is formed on the ferroelectric film 19 by carrying out sputtering in an oxygen content ambient atmosphere using the target 30 of platinum and lead.

[0048] the lead 33 of the shape of a sheet whose thickness it is 1mm around on the 6 inches (however, 1 inch about 2.54cm) platinum target 31, and is 2mm here -- 17 sheets -- mutual -- etc. -- carrying out -- it is -- spacing -- with, it arranges (refer to drawing 2 .). As for this lead sheet 33, purity uses 99.99% or more of thing. Moreover, an area of one sheet of the lead sheet 33 is made into about 5% of the area of the platinum target 31. In order to make it not degrade the crystallinity of platinum, as for the area of the lead sheet 33, it is desirable to carry out to about 5% of the platinum target 31 as mentioned above. Moreover, what is necessary is just to carry the lead sheet 33 on the platinum target 31. Thus, what has arranged the lead sheet 33 is used as a target 30 on the platinum target 31.

[0049] Next, sputtering is performed in an oxygen content ambient atmosphere using this target 30.

[0050] Alignment of the substrate 10 equipped with a target 30, the ferroelectric film 19, and the lower electrode 17 is carried out, and it installs in a sputtering

system. Sputtering is performed using the argon sputtering gas containing oxygen 10 capacity %. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time. After performing a pre spatter for 2 minutes, the platinum electrode 21 containing the lead whose thickness is 200nm and which is about 10% is formed on the ferroelectric film 19 by opening and carrying out sputtering of the shutter for 3 minutes.

[0051] Thereby, the sample of the gestalt of this operation is formed (refer to drawing 1 ).

[0052] As the gestalt of the 1st operation explained, a platinum electrode has a possibility of generating a reactant high hydrogen atom and returning the ferroelectric film, in heat treatment under the ambient atmosphere of reducibility. And reduction of the ferroelectric film has arisen mainly from the interface of an up electrode and the ferroelectric film.

[0053] With the gestalt of this operation, the platinum electrode which lead contained is used as an up electrode. In other words, an impurity called lead is contained in the platinum electrode. For this reason, the property which absorbs the hydrogen of a platinum electrode has deteriorated. Therefore, since generating of a reactant high hydrogen atom can be suppressed in connection with this, even if it performs heat treatment by reducing atmosphere which contains hydrogen, a possibility of degrading the property of the ferroelectric film disappears.

[0054] Moreover, in this up electrode, if lead is contained about 2% to about 20%, effectiveness will be acquired as an impurity. That is, the property of absorbing the hydrogen in the reducing atmosphere of a platinum electrode, and generating a reactant high hydrogen atom can be degraded. It is good to consider as 10% preferably as a rate which lead contains.

[0055] Moreover, although there is a possibility that a constituent may be spread from an up electrode and the ferroelectric film may be polluted with heat treatment performed into the production process of ferroelectric random-access memory, since an up electrode is an electrode which consisted of platinum and lead which is the constituent of the titanate-acid lead zirconate film of the ferroelectric film, there is no possibility of making the ferroelectric film polluting here.

[0056] Moreover, although lead and platinum constituted the up electrode from the gestalt of this operation, you may constitute from Ti and platinum which are the constituent of the titanate-acid lead zirconate film, and the same effectiveness is acquired even if constituted from a zirconium and platinum.

[0057] Moreover, with the gestalt of this operation, although platinum is used for

the ingredient of an electrode, \*\*\*\*\* of Ru, Rh(s), Pd, Os(es), and Ir(s) which are the platinum group which has the same property as platinum may be used as an electrode material. Especially, Ir and Ru are easy to etch compared with platinum, and since it excels in workability, it is thought that it is an ingredient desirable as an electrode material.

[0058] It heat-treats in an oxygen content ambient atmosphere to the sample of the ferroelectric random-access memory formed with the gestalt of <gestalt of the 3rd operation> the 2nd operation.

[0059] As the gestalt of the 2nd operation explained, after carrying out the laminating of a polish recon layer and the TiN barrier layer one by one and forming a substrate on a silicon substrate, on this substrate, sequential formation of the up electrode as the 2nd electrode containing the lower electrode, the titanate-acid lead zirconate film and platinum, and lead of platinum as the 1st electrode is carried out, and a sample is formed.

[0060] Then, in the gestalt of this operation, after putting in this sample into the ambient atmosphere which is about 100% oxygen, heat-treatment is performed at the temperature of 800 degrees C for 30 minutes.

[0061] Consequently, in an up electrode, the component which constitutes this film is further spread from the ferroelectric film. Therefore, the property which absorbs the hydrogen of an up electrode can be degraded further. Thereby, further improvement in the resistance of the ferroelectric film to heat treatment by reducing atmosphere can be aimed at.

[0062] if extent as atmospheric air with the same oxygen contains the oxygen content ambient atmosphere of heat-treating, 20% or more -- \*\*\*\* -- \*\*\*\*ing . As the rate which oxygen contains is high, it is more desirable.

[0063] Moreover, in the gestalt of this operation, although temperature of heat-treatment was made into 800 degrees C, it can carry out at the temperature of 600 degrees C - 850 degrees C. It is good to heat-treat preferably at the temperature within the limits of 750 degrees C - 800 degrees C.

[0064] With reference to drawing 3 , it explains about the sample of the ferroelectric random-access memory of the gestalt of <gestalt of the 4th operation> the 4th operation. Drawing 3 is the sectional view showing the 4th rough configuration of the sample of the gestalt of operation.

[0065] It explains hereafter per [ which is different from the gestalt of the 1st - the 3rd operation ] point, and the detailed explanation is omitted about the same point.

[0066] As for this sample, the up electrode 21 is formed as the lower electrode 17, the ferroelectric film 19, and the 2nd electrode as the 1st electrode on the

substrate 10. Furthermore, the interlayer 23 who contains a kind or two sorts or more of elements and oxygen among the elements which constitute the ferroelectric film 19 is formed between the ferroelectric film 19 and the up electrode 21 ( drawing 3 ).

[0067] This sample is manufactured as follows.

[0068] Like the gestalt of the 1st operation, on a silicon substrate 11, the laminating of the polish recon layer 13 and the TiN barrier layer 15 is carried out one by one, and a substrate 10 is formed.

[0069] Next, like the gestalt of the 1st operation, after forming the lower electrode 17 of platinum, the titanate-acid lead zirconate film is formed as ferroelectric film 19 on this lower electrode 17.

[0070] Then, the interlayer 23 containing lead and oxygen is formed with the gestalt of this operation.

[0071] Here, sputtering is performed in an oxygen content ambient atmosphere using a 6 inches lead target. Bi target and the structure by which the lower electrode 17 and the ferroelectric film 19 were formed on the substrate 10 are installed in a sputtering system, and sputtering is performed using the argon sputtering gas containing oxygen 10 capacity %. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time. After performing a pre spatter for 2 minutes, the interlayer 23 containing 20nm lead and oxygen is formed on the ferroelectric film 19 by opening and carrying out sputtering of the shutter for 20 seconds.

[0072] Then, sputtering is performed using the argon sputtering gas containing oxygen 10 capacity % using a 6 inches platinum target. 7mTorr(s) and spatter power are made to 500kW, and substrate temperature is made into 300 degrees C for the gas pressure of the sputtering gas at this time.

[0073] After performing a pre spatter for 2 minutes, a shutter is opened, sputtering is performed for 3 minutes, and the up electrode 21 of platinum with a thickness of 200nm is obtained.

[0074] Thereby, the sample of the gestalt of the 4th operation is formed (refer to drawing 3 ).

[0075] When an interlayer insulation film and the passivation film tend to be further formed in this sample and it is going to manufacture ferroelectric random-access memory, the process which performs heat treatment under reducing atmosphere is not avoided. Under reducing atmosphere which contains hydrogen, the up electrode of platinum absorbs the hydrogen in an ambient atmosphere, and generates a reactant high hydrogen atom. This hydrogen atom

makes the ferroelectric film return, and has become one of the causes which degrades the property of film, such as film fatigue. What is easy to be influenced of a reactant high hydrogen atom, namely, is easy to be returned is near the interface of the ferroelectric film and an up electrode.

[0076] For this reason, if the layer containing oxygen is prepared between the ferroelectric film 19 and the up electrode 21 as an interlayer 23 like the gestalt of this operation, it can prevent that inside [ this ] \*\*\*\* 23 turns into a barrier layer, and a hydrogen atom attains to the ferroelectric film 19 from the up electrode 21. Therefore, even if it performs heat treatment by reducing atmosphere, degradation of the property of the ferroelectric film 19 can be controlled.

[0077] Moreover, even if this interlayer's 23 thickness is thick, it is good to be referred to as 50nm. If it is 50nm or less in thickness, the up electrode 21 and the ferroelectric film 19 are not insulated by the interlayer 23 who is an oxide film, and the effect of the hydrogen atom from the up electrode 21 to the ferroelectric film 19 can be controlled.

[0078] Moreover, the middle class 23 is a layer containing the lead of the constituent of the titanate-acid lead zirconate film which is the ferroelectric film 19. For this reason, even if the component which constitutes an interlayer 23 from an interlayer 23 to the ferroelectric film 19 is spread by heat treatment performed into a ferroelectric-random-access-memory production process, there is no possibility that the ferroelectric film 19 may be polluted.

[0079] Moreover, the effectiveness that the middle class 23 is the same also as the layer containing Ti which constitutes not only the layer containing lead and oxygen but the titanate-acid lead zirconate film 19, and oxygen, or a layer containing a zirconium and oxygen is acquired.

[0080] Moreover, in the gestalt of this operation, although the up electrode 21 is used as the platinum electrode, it is good also as an electrode of Ru, Rh, Pa, Os, and Ir which are the platinum group metals which have the same property not only as this but platinum.

[0081] It heat-treats in an oxygen content ambient atmosphere to the sample of the ferroelectric random-access memory formed with the gestalt of <gestalt of the 5th operation> the 4th operation.

[0082] As the gestalt of the 4th operation explained, after carrying out the laminating of a polish recon layer and the TiN barrier layer one by one and forming a substrate on a silicon substrate, on this substrate, sequential formation of the lower electrode of platinum, the titanate-acid lead zirconate film, an interlayer, and the up electrode of platinum is carried out, and a sample is formed.

[0083] Then, in the gestalt of this operation, after putting in this sample into the



ambient atmosphere of about 100% oxygen, heat-treatment is performed for 30 minutes at the temperature of 800 degrees C.

[0084] Consequently, lead is spread from an interlayer in an up electrode. For this reason, since an impurity is introduced into the up electrode of platinum, the property which absorbs the hydrogen of a platinum electrode can be degraded. Therefore, since generating of a reactant high hydrogen atom can be suppressed, even if it heat-treats to this sample in reducing atmosphere, the ferroelectric film can control degradation of the film accompanying this, without being returned. Even if a hydrogen atom occurs, the effect of the hydrogen atom to the ferroelectric film can be suppressed by the interlayer.

[0085] if extent as atmospheric air with the same oxygen contains the oxygen content ambient atmosphere of heat-treating, 20% or more -- \*\*\*\* -- \*\*\*\*ing . As the rate which oxygen contains is high, it is more desirable.

[0086] Moreover, in the gestalt of this operation, although temperature of heat-treatment was made into 800 degrees C, it can carry out at the temperature of 600 degrees C - 850 degrees C. It is good to heat-treat preferably at the temperature within the limits of 750 degrees C - 800 degrees C.

[0087] In the sample of the ferroelectric random-access memory of the gestalt of this operation, although platinum is used for the ingredient of an electrode, platinum group metals, such as not only this but Ru, Ir, etc., may be used.

---

[Translation done.]

**\* NOTICES \***

**Japan Patent Office is not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

[Brief Description of the Drawings]

[Drawing 1] It is the 1st and the configuration explanatory view of the sample of the ferroelectric random-access memory of the gestalt of the 2nd operation, and is drawing showing the cut end of a rough cross section.

[Drawing 2] It is the rough block diagram of the target used for sputtering.

[Drawing 3] It is drawing of the cut end of a cross section showing the rough configuration of the sample formed with the gestalt of the 4th operation.

[Description of Notations]

10: Substrate

11: Silicon substrate

13: Polish recon layer

15: TiN barrier layer

17: The 1st electrode (lower electrode)

19: Ferroelectric film

21: The 2nd electrode (up electrode)

23: Interlayer

30: Target

31: Platinum target

43: Sheet-like lead (lead sheet)

---

[Translation done.]

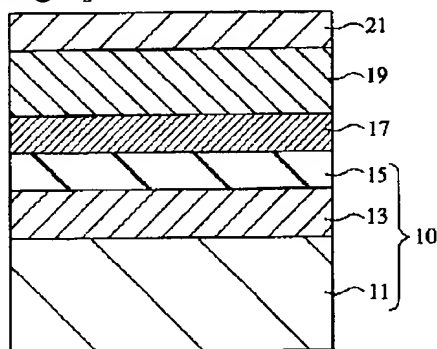
# \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## DRAWINGS

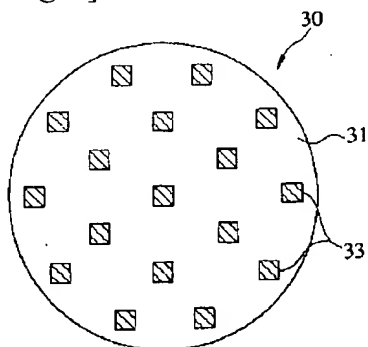
[Drawing 1]



- |                         |             |
|-------------------------|-------------|
| 10: 下地                  | 11: シリコン基板  |
| 13: ポリシリコン層             | 15: TaNバリア層 |
| 17: 第1電極 (下部電極)         |             |
| 19: 強誘電体膜 (チタン酸ジルコン酸鉛膜) |             |
| 21: 第2電極 (上部電極)         |             |

第1および第2の実施の形態の構成説明図

[Drawing 2]

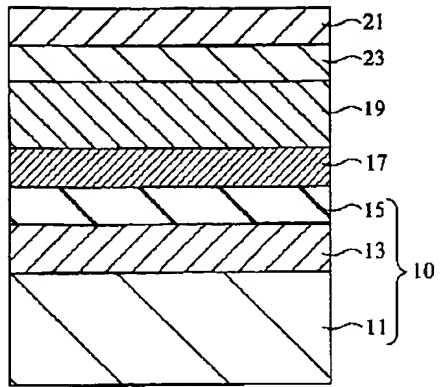


- |                   |             |
|-------------------|-------------|
| 30: ターゲット         | 31: 白金ターゲット |
| 33: シート状の鉛 (鉛シート) |             |

ターゲットの概略図

第 4 の実施形態

[Drawing 3]



23：中間層

第 4 の実施形態の形態

---

[Translation done.]